

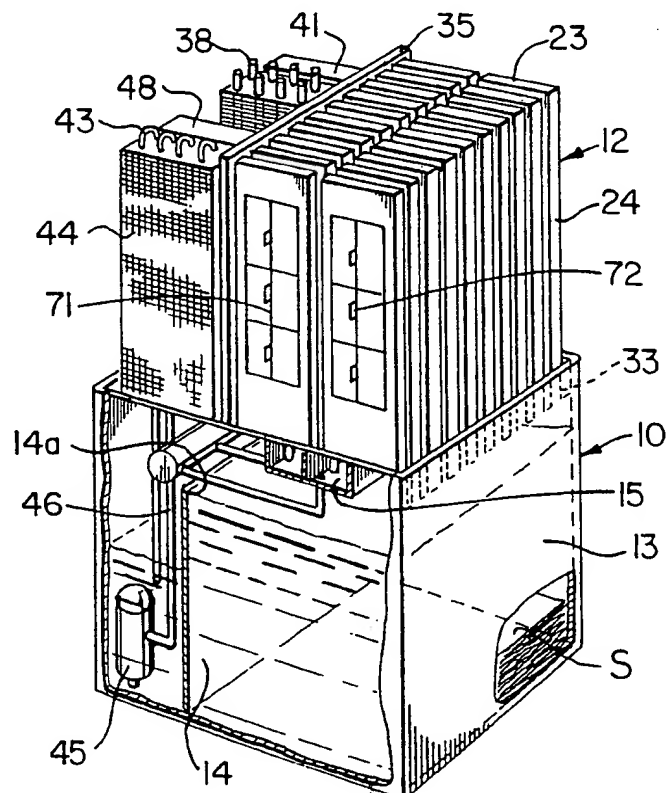
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : H01M 6/50, 12/06		A1	(11) International Publication Number: WO 90/11625
			(43) International Publication Date: 4 October 1990 (04.10.90)
(21) International Application Number: PCT/CA90/00096 (22) International Filing Date: 22 March 1990 (22.03.90) (30) Priority data: 594,668      23 March 1989 (23.03.89)      CA (71) Applicant (for all designated States except US): ALCAN INTERNATIONAL LIMITED [CA/CA]; 1188 Sherbrooke Street West, Montreal, Quebec H3A 3G2 (CA). (72) Inventor; and (75) Inventor/Applicant (for US only) : O'CALLAGHAN, Wilfrid, Bernard [CA/CA]; 97 Westmoreland Road, Kingston, Ontario K7M 1J6 (CA). (74) Agents: EADES, Norris, M. et al.; Kirby, Eades, Gale, Baker & Potvin, Box 3432, Station D, Ottawa, Ontario K1P 6N9 (CA).		(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

**(54) Title:** METAL/AIR BATTERY WITH SEEDED RECIRCULATING ELECTROLYTE

**(57) Abstract**

A battery and a method for its operation are described. The battery comprises a metal-air battery with an air cathode having opposed surfaces supported for simultaneous exposure of a first surface to air and a second surface to liquid electrolyte and a metal anode positioned in spaced juxtaposed relation to the second cathode surface to define therewith an anode-cathode gap for receiving electrolyte to form an anode-cathode pair electrically coupled by electrolyte. The battery contains an alkaline electrolyte and seed particles adapted to decrease passivation of the anode during discharge of the battery.



### DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

#### *FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

Metal/air battery with seeded recirculating electrolyteBackground of the Invention

The invention relates to metal/air batteries and methods for their operation, and particularly such  
5 batteries having recirculating electrolyte containing a particulate seeding agent.

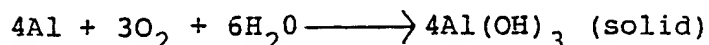
Metal/air batteries produce electricity by the electro-chemical coupling of a reactive metallic anode to an air cathode through a suitable electrolyte in a cell. The air  
10 cathode is typically a sheet-like member, having opposite surfaces respectively exposed to the atmosphere and to the aqueous electrolyte of the cell. During cell operation oxygen is reduced within the cathode while metal of the anode is oxidized, providing a usable electric current  
15 flow through external circuitry connected between the anode and cathode. The air cathode must be permeable to air but substantially impermeable to aqueous electrolyte, and must incorporate an electrically conductive element to which the external circuitry can be connected. Present-day  
20 commercial air cathodes are commonly constituted of active carbon (with or without an added dissociation-promoting catalyst) in association with a finely divided hydrophobic polymeric material and incorporating a metal screen as the conductive element. A variety of anode metals have been  
25 used or proposed; among them, zinc, alloys of aluminum and alloys of magnesium are considered especially advantageous for particular applications, owing to their low cost, light weight, and ability to function as anodes in metal/air battery using a variety of electrolytes.

30 A typical aluminum/air cell comprises a body of aqueous electrolyte, a sheet-like air cathode having one surface exposed to the electrolyte and the other surface exposed to air, and an aluminum alloy anode member (e.g. a flat plate) immersed in the electrolyte in facing spaced  
35 relation to the first-mentioned cathode surface.

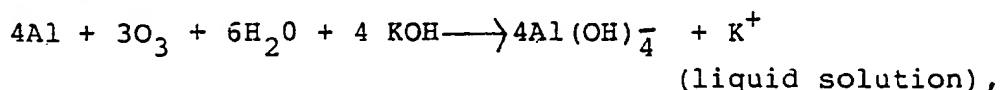
**SUBSTITUTE SHEET**

Aqueous electrolytes for metal-air batteries consist of two basic types, namely a neutral-pH electrolyte and a highly alkaline electrolyte. The neutral-pH electrolyte usually contains halide salts and, because of its relatively low electrical conductivity and the virtual insolubility of aluminum therein, is used for relatively low power applications. The highly alkaline electrolyte usually consists of NaOH or KOH solution, and yields a higher cell voltage than the neutral electrolyte.

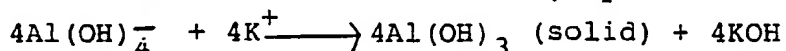
In neutral-pH electrolyte, the cell discharge reaction may be written:



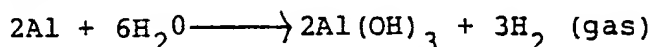
In alkaline electrolyte, the cell discharge reaction may be written:



followed, after the dissolved potassium (or sodium) aluminate exceeds saturation level, by:



In addition to the above oxygen-reducing reactions, there is also an undesirable, non-beneficial reaction of aluminum in both types of electrolyte to form hydrogen, as follows:

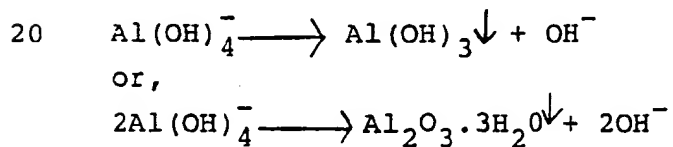


There is a need for a metal-air battery which can be used as an emergency power source at locations where electric supply lines do not exist. Such a battery must have a high energy capacity and a high power density and be capable of running for a long period of time under high load, e.g. deliver 500 watts with an energy density in excess of 365 Wh/kg. During discharge of a battery containing aluminum anodes and caustic electrolyte, the concentration of dissolved aluminum in the electrolyte continues to build up until a limiting level of super-saturation is reached such that no more aluminum from the anode can enter into solution. At this point a film or

**SUBSTITUTE SHEET**

scale of aluminum hydroxide forms on the anode surface causing passivation of the anode and collapse of the battery voltage.

The solubility of aluminum hydroxide increases with temperature and with caustic concentration. In metal-air batteries, caustic concentrations are chosen to maximize electrical conductivity and are typically in the range of 4-5 molar. At this caustic level the aluminum solubility at the prevailing battery temperature of 55-75°C, corresponds to a molar ratio of dissolved Al to KOH or NaOH of roughly 0.40. Aluminum may continue to dissolve above this ratio into the supersaturated zone and even attain a ratio as high as 0.80. In the supersaturation zone the solution is in a metastable state and has a natural tendency to reduce its dissolved aluminum concentration by precipitating out solid aluminum-oxide trihydrate or bayerite according to the following equation:



The metastable state possesses great stability and the Al/XOH ratio can go as high as 0.75-0.80, where anode passivation occurs.

Various techniques have been tried to avoid passivation at high energy capacities and high energy densities and one technique has been to use a very large volume of electrolyte. However, this greatly increases the battery size and weight, while reducing its energy density and market desirability. Another way of extending discharge time prior to passivation has been to use higher caustic concentrations, but this has the effect of reducing electrolyte conductivity and hence battery voltage. Yet another way has been to add organic stabilizers to the electrolyte to improve the meta-stability, or to use

**SUBSTITUTE SHEET**

NaOH/KOH mixtures to achieve the same effect, but these methods achieve only a relatively small extension of the battery capacity.

It is an object of the present invention to develop a battery capable of long time operation under high load without the problem of anode passivation.

#### Summary of the Invention

According to the present invention it has been discovered that the above passivation problem in metal-air batteries with alkaline electrolyte can be overcome by the addition to the electrolyte of a seed material, such as aluminum oxide or salt. This seed material preferably has a relatively large surface area per unit mass and is advantageously added to the electrolyte after the electrolyte is approaching saturation.

In the supersaturation zone, the driving force for the precipitating out of solid aluminum-oxide trihydrate or bayerite increases with the square of the supersaturation level, and the rate of the precipitation reaction is directly proportional to the surface area of the seed present. Tests in NaOH electrolyte have shown the reaction rate to be:

$$\text{Precipitation Rate} = 5.05 \times 10^7 \cdot A \cdot \text{Exp}(-14,155/RT) \cdot ((R - R_e)/(1 - R))^2$$

grams Al per minute

Where A = Seed surface area in square meters

R = Moles Al/moles NaOH

R<sub>e</sub> = Equilibrium ratio: moles Al/moles NaOH

The above equation shows that the presence of seed in the electrolyte is essential to achieve a precipitation rate that is fast enough to avoid the high supersaturation levels that cause anode passivation.

The seed material preferably has very small particle sizes, e.g. less than 1 micron. These very small particles move freely through the battery with the flow of electro-

# SUBSTITUTE SHEET

-5-

lyte and have been found to be highly effective in preventing anode passivation. While a variety of different materials may be used as seed, including aluminum oxides and salts, the mineral gibbsite has been found to be especially effective. It has also been found that  $\alpha$ -alumina is a very effective seeding agent, particularly when held in suspension, e.g. by stirring.

Because of the very small particle size of the seed used, there is a danger that the seed may dissolve in fresh electrolyte. Accordingly, it is preferred to add the seed to the electrolyte after several hours of battery discharge when the electrolyte is approaching saturation in dissolved aluminum. Once the electrolyte has reached saturation, there is no longer a problem of seed dissolution.

Thus, one feature of the present invention is a method for operating a metal-air battery of the type comprising an air cathode having opposed surfaces supported for simultaneous exposure of a first of said surfaces to air and a second of said surfaces to liquid electrolyte and a metal anode positioned in spaced juxtaposed relation to said second cathode surface to define therewith an anode-cathode gap for receiving electrolyte to form an anode-cathode pair electrically coupled by electrolyte. According to this invention, seed particles preferably having sizes of less than 1 micron are added to the electrolyte within the battery. The seeds are used in sufficient quantity to decrease passivation of the anode during discharge of the battery. Preferably the seeds are added to the electrolyte after the battery has been discharging for a period of time such that the electrolyte is approaching saturation.

The seed particles may be added manually to the electrolyte in the battery, but they may also be held in a releasable container within the battery which container is adapted to release the seeds into the electrolyte after a specific quantity of electrical current has been passed by

**SUBSTITUTE SHEET**

the battery, i.e. after a predetermined number of  
ampere-hours. The release mechanism of the container is  
adapted to be actuated by an accumulator which responds to  
the current production of the battery. Thus, the device  
5 counts time during which a known current is being produced  
or both time and current. When the predetermined total  
operating time or ampere-hours has been reached, the  
container releases the seeds into the electrolyte.

With the above system, the battery may stop and start  
10 several times before electrolyte saturation is reached and  
the seeds are not released until the total ampere-hours is  
such that the electrolyte is near saturation. Of course,  
at that point there is no longer any problem with the  
seeds remaining in the electrolyte even when the battery  
15 is stopped because the tendency for dissolution of the  
seeds substantially ends as the electrolyte reaches  
saturation.

The  $\alpha$ -alumina is totally insoluble in caustic, but is  
an effective seeding agent. It can be dumped into the  
20 electrolyte when filling the battery and allowed to settle  
on the floor of the reservoir where it remains throughout  
the shelf life of the battery. A stirring device is  
included in the reservoir so that when the  $\alpha$ -alumina is  
required as seeding agent, the stirring device is started  
25 to hold the  $\alpha$ -alumina particles in suspension.

The invention is of particular interest for use in  
batteries characterized by a supply reservoir for the  
electrolyte enclosed in a housing below a plurality of  
metal-air cells mounted in side-by-side relationship with  
30 air gaps therebetween. Each of the above cells comprises  
a pair of spaced-apart flat side walls joined by edge  
faces. The flat side walls include air cathodes and a  
metal anode is mounted between the flat side walls con-  
taining the air cathodes in facing spaced relationship to  
35 the cathode surfaces. Each cell includes an electrolyte  
inlet connection in a lower region below the bottom of the

**SUBSTITUTE SHEET**



anode and an electrolyte outlet connection. The inlet connector is flow connected to pump means for pumping electrolyte from the reservoir and the outlet connector is adapted to return electrolyte to the reservoir. The  
5 battery is normally completed by circuit means for connecting the cells in series to each other and to an external load. With this battery, the seeds are preferably added to the electrolyte in the reservoir.

The metal-air cells are typically placed on a support  
10 panel with electrolyte inlet and outlet connectors extending through the panel. The electrolyte is pumped upwardly through the inlet connectors and into the metal-air cells.

The outlet connectors extend through the support panel  
15 at locations such that the returning electrolyte can flow directly into the electrolyte reservoir.

Each metal-air cell preferably includes a vertical divider wall extending from the bottom edge face up to a short distance below the top edge face. This divider wall  
20 provides an electrolyte chamber connected to the electrolyte inlet and an overflow chamber connected to the electrolyte outlet. The top end of the divider wall forms an electrolyte overflow weir and is positioned at or above the top end of the metal anode. With this arrangement,  
25 the electrolyte flows upwardly through the metal-air cells and provides a strong flushing action to remove metal hydroxide reaction products formed in the space between the anode and cathode. Thus, metal hydroxide product is carried upwardly and over the weir for discharge back into  
30 the reservoir. This reaction product settles to the bottom of the reservoir and the battery can be operated for a considerable period of time before it is necessary to remove the collected solid reaction product from the bottom of the reservoir.

35 The electrolyte reservoir preferably includes a divider wall which extends upwardly for part of the height

**SUBSTITUTE SHEET**

of the reservoir to provide a further overflow weir. The electrolyte flowing over the internal weir of the reservoir is substantially free of the solid reaction product and pump inlets are positioned in the reservoir on the downstream side of the weir.

The electrolyte pump may be in the form of a single pump or several small centrifugal pumps may be used. When a single pump is used, it is preferably in the form of a column pump with an impeller submersed in the electrolyte in the reservoir on the downstream side of the weir and a motor mounted above the electrolyte. The single pump can be used with a single large discharge pipe and no manifold. When several pumps used, they are are preferably submersible centrifugal pumps which are mounted in the reservoir on the downstream side of the weir. These pumps discharge into a first holding tank or manifold from which a plurality of connector lines connect to the manifold positioned beneath the inlets to the metal-air cells.

In order to intensify the supply of air to the gaps between the metal-air cells, a blower and air distributor are preferably installed adjacent the cells to blow air through the gaps. According to a preferred feature, this air is used for a secondary purpose of flushing the surface of the electrolyte in the reservoir. It has been found that in high load batteries of this type, there can be build-up of hydrogen on the surface of the electrolyte and this can reach explosive levels. To avoid this problem and dilute the hydrogen concentration in the reservoir, openings are preferably provided in the support panel between the metal-air cells at the side of the cells remote from the blower. In this manner, the air passing in one direction through the gaps between the cells is forced down through the openings in the support panel and across the surface of the electrolyte in the reverse direction, thereby diluting the hydrogen. This air can then be discharged through a demister and a condenser to the

**SUBSTITUTE SHEET**

atmosphere.

Also, to control the temperature of the electrolyte, a heat exchanger may be provided through which electrolyte is recirculated from the reservoir. When high electrical outputs are required from the battery, the condenser can be replaced by a second heat exchanger and the air can be discharged directly to the atmosphere.

These and many other features and advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings wherein:

Figure 1 is a schematic view of a metal-air battery with covers removed;

Figure 2 is a perspective view of a cover for the metal-air cells;

Figure 3 is a perspective view of a cover for the condenser and heat exchanger;

Figure 4 is a further schematic illustration of the battery;

Figure 5 is a top plan view of the battery with cover removed;

Figure 6 is a cross-sectional view of a metal-air cell;

Figure 7 is a plot of Al/KOH ratio as a function of discharge time;

Figure 8 is a plot of volts and amps as a function of discharge time;

Figure 9 is a plot of volts and amps as a function of discharge time; and

Figures 10, 11 and 12 are three different plots of voltage as a function of discharge time;

Referring now to the drawings, a housing 10 with side walls 13 is provided comprising a suitable material resistant to caustic solutions at temperatures up to 95°C, such as polypropylene or 316 stainless steel, and serving as an electrolyte reservoir. Extending across an upper

**SUBSTITUTE SHEET**

region of the interior of housing 10 is a support panel or platform 11. At one side of the housing, there are gaps 36 in the support panel, providing air openings into the electrolyte reservoir.

5        Extending upwardly from and supported by the support panel 11 are a plurality of metal-air cells 12 with air gaps therebetween. These cells 12 have a long, flat rectangular shape with side walls 21 having window openings retaining air cathodes 22.

10        The air cathodes 22 are generally rectangular sheet members fabricated of activated carbon and incorporating an electrically conductive material such a wire mesh. Each cathode 22 extends entirely over an opening in wall 21 with its edges sealingly adhered to the interior  
15        surface of the wall around the periphery of the opening. The cathodes in the two side walls are preferably electrically connected such that they effectively form a single cathode surrounding the anode spaced between them. The cathodes are susceptible to hydrostatic deformation  
20        which affects the gap between the anode and cathode. To avoid this problem, a supporting grid 71 is provided across the opening in wall 21 and small projections 72 are provided on the outer edges of the grid 71. These  
25        projections 72 are arranged so that the projections of adjacent pairs of cells engage each other, thereby providing a rigid structure while permitting free flow of air between the cells.

30        The side walls 21 are joined by a removable top lid 23, a pair of end walls 24 and a bottom wall 25, the lid 23 tightly sealing within walls 21 and 24. The anode 26 has a vertically extending tab 75 projecting upwardly through a slot in lid 23, and similarly the cathode has a connector lead 76 extending from the side of the cell where  
35        the two cathodes are joined. The tab 75 and lead 76 are connected to suitable circuit means (not shown) for connecting the cells in series to each other and to an

**SUBSTITUTE SHEET**

external load.

A divider wall 30 is formed between side walls 21 near one end wall 24 to form a narrow discharge conduit 32 adjacent the side edge. This divider wall 30 terminates at an upper edge 31 a short distance below the cell top edge 23, the edge 31 forming an overflow weir. Vertical slots are provided in divider wall 30 and side wall 24 to retain an aluminum anode 26. This anode terminates slightly below the top edge 31 of divider wall 30. An inlet tube 27 connects to bottom edge 25 beneath the anode 26 and an outlet tube 33 connects to bottom edge 25 directly below the discharge conduit 32. These pass through holes 29 and 29a respectively in support panel 11. Preferably the tube 27 is provided with annular grooves containing O-rings which snugly seal the tube 27 within hole 29. The discharge tube 33 is formed slightly smaller than hole 29a to facilitate inserting and withdrawing the metal-air cell 12. To prevent leakage of air through holes 29a, a thin foam or rubber pad with small holes may be placed on the panel 11 over the holes 29a. The discharge tubes pass through the small holes in the pad and then through the larger holes 29a.

Immediately below the inlet tubes 27 is mounted a manifold or manifolds 15 extending across beneath support panel 11. Preferably there is a divider wall 50 providing two manifolds, one for each aligned row of metal-air cells. As shown in Figure 3, four inlet tubes 16 feed into the manifold 15, two of these tubes feeding into one half of the manifold and two into the other half. The inlet end of the four tubes 16 connect to a second manifold 17 which in turn connects to three submersible centrifugal pumps 19 by way of outlet lines 18. Two of the three outlet lines 18 are provided with reverse flow check valves 49. The pumps 19 have inlets 20 which are preferably positioned well above the bottom of the electrolyte reservoir. All tubing, connectors and

**SUBSTITUTE SHEET**

-12-

manifold are preferably made of a non-conducting material in order to reduce possible shunt currents.

The electrolyte reservoir preferably has a divider wall 14 with an upper edge 14a forming an overflow weir.

5 As can be seen from Figure 1, the electrolyte will, after some discharge time has elapsed, have a higher level to the right of the weir and a lower level to the left of the weir. Partially clarified electrolyte overflows from the right side to the left side of the weir.

10 Inlets 20 for pumps 19 are positioned in the downstream side of the reservoir for pumping partially clarified electrolyte up through manifolds 17 and 15 and through the metal-air cells 12. The electrolyte travels from the manifold 15 in an upward direction through the gaps between the  
15 anode and cathodes simultaneously flushing any reaction product formed in the gaps. The electrolyte with reaction product is carried over the weir 31 and down discharge conduit 32 and outlet 33 back into the upstream side of the electrolyte reservoir. The reaction product S settles  
20 to the bottom of the upstream side with the partially clarified electrolyte flowing over the weir for recycle through the metal-air cells.

An air distributor wall 35 is provided adjacent the metal-air cells 12 with openings 66 opposite the gaps  
25 between the cells for discharge of air through the gaps. A blower 34 feeds air to the distributor wall 35, this blower being powered by electricity generated by the battery. In operation, the compartment containing the metal-air cells is sealed within a cover as shown in  
30 Figure 2 except for the air inlets 66 and the gaps 36 in the support panel 11. This compartment cover includes the air distributor wall 35, a pair of side walls 56, an end wall 57 opposite wall 35 and a removable lid 58. The walls 35, 56 and 57 are tightly sealed together and the  
35 bottom edges of the four walls are tightly sealed to the top of the housing 10, while the lid 58 is tightly

**SUBSTITUTE SHEET**

connected to the top edges of the four walls. Alternatively, the lid 58 may be sealed to the walls and the entire compartment cover may be removable. Thus, when the blower 34 is in operation, air is blown across through the gaps between the metal-air cells 12 and down through the support panel openings 36 into the reservoir. The air then travels in the reverse direction across the surface of the electrolyte in the reservoir, picking up hydrogen, and is discharged to the atmosphere upwardly through a plurality of metal tubes 38 of condenser 37. Heat exchange in the condenser is enhanced by means of a plurality of mechanically bonded metal fins 39 through which air is blown from fans 41. Alternatively, the condenser may be water cooled.

The electrolyte may be cooled by means of a heat exchanger 42, the heat exchange taking place between metal tubes and metal fins by way of air fans 48. The electrolyte is pumped by way of pump 45 upwardly through tube 46, through the heat exchanger and is discharged back into the reservoir via discharge line 47. The operation of the heat exchanger fans is controlled by a thermal switch set to a predetermined temperature.

The condenser and heat exchanger may be protected by a cover 60 as shown in Figure 3 and consisting of two sides 61, one end wall 63 and a top wall 64. Side walls 61 contain openings 62 to permit free flow of air around the condenser, heat exchanger and circulating air blower. The top wall 64 has an outlet 65 serving as an exhaust from condenser tubes 38. This outlet 65 may be connected to an exhaust vent.

A small auxilliary battery is used to start the battery of the invention, this auxilliary battery being connected to the pumps 19. Thus, when the pumps 19 are activated, they commence pumping electrolyte upwardly through manifolds 17 and 15. Since gas may accumulate in the manifolds, it is desirable to provide a means for venting

**SUBSTITUTE SHEET**

gas before it passes upwardly through the metal-air cells by providing small holes in the upper regions of the side walls 51 of manifold 15. After the gas is fully eliminated from the manifold, there continues to be a slight flow of electrolyte through the holes. As soon as the electrolyte makes contact between the anode and cathode, electricity generation commences and the auxilliary battery is no longer required. The pumps 19 and 45, the blower 34 and the fans 41 and 48 are all driven by excess power from the battery of the invention. It is also possible to provide a manual pumping device to start the battery, thereby avoiding the need for the auxilliary battery.

The three pumps 19 provide a sufficiently excess flow capacity that two of the three pumps can fail and sufficient electrolyte will still be pumped to fill the metal-air cells with electrolyte and keep the battery operational. In order to prevent a flow short circuit through a failed pump, reverse flow check valves 49 are provided on all except one pump.

When it is desired to stop the battery for any reason, such as replacing the metal-air cells, it is simply a matter of stopping the pumps whereby the electrolyte drains out of the metal-air cells and the cells can be replaced. Thus, the battery can be placed back into immediate operation and individual cells can be opened and the anodes replaced at a convenient time.

In order to flush the system, a one-way discharge valve outlet may be provided in a side wall 13 of housing 10 at a level above the highest permissible accumulation of reaction product solids 5 and below the level of weir 14a. Thus, with the one-way valve in the open position, water can be fed into the pump side of the electrolyte reservoir and then circulated through the pumps and cells into the upstream side of the electrolyte reservoir. Simultaneously, liquid flows from the reservoir out through the one-way valve. In this manner, all caustic except for

**SUBSTITUTE SHEET**



that held within the solids deposit S may be flushed out of the battery.

A battery of the design shown in Figures 1-6 was produced with 20 aluminum-air cells. Each aluminum anode had a thickness of 13 mm, a height of 18.2 cm and a width of 11.1 cm. The cathodes used were type AE-20 gas-diffusion cathodes made by Electromedia Inc. The cells each had a thickness of 1.7 cm, a height of 23.0 cm and a width of 13.0 cm.

The electrolyte was 5 M KOH with 0.005 M sodium stannate and it was pumped through the aluminum-air cells at a flow rate of 15 l/min. Air was circulated between the cells and through the reservoir at a rate of about 28 l/min. This battery provided over 500 watts continuously for more than 60 hours with an output current of approximately 19 amps. The battery also had a net energy output of over 300 watt-hours per kg of battery weight.

In order to determine how the Al/KOH ratio behaves as a function of discharge time, a computer simulation was carried out based on the equation shown on page 4 at 72.5 watts per cell and seed additions of 3.30 and 60 grams. The results are shown in Figure 7 and it can be seen that the higher the seed charge and the earlier it is added, the lower the maximum Al/KOH ratio attained. Because the electrical conductivity of the solution diminishes as the Al/KOH ratio increases, the effect of the seed additions is reflected in the cell voltage as represented by the family of full line curves in Figure 7.

It has been determined that if sufficient seed is added to keep the Al/XOH ratio below 0.60, current densities as high as 180 mA/cm<sup>2</sup> are possible without anode passivation and that to maintain a current density of 60 mA/cm<sup>2</sup>, sufficient seed to maintain the ratio below 0.70 is all that is required.

**SUBSTITUTE SHEET**

Even if the anode does not passivate, there is a further problem with the occurrence of very high supersaturation levels corresponding to Al/XOH ratios above 0.70 and that is the uncontrolled nucleation of a vast number of new particles of solid aluminum hydroxide, probably close to the anode surface. These have the effect of increasing the viscosity of the electrolyte to that of a thick soup and thereby clogging the cell and causing battery failure. With sufficient seed present to avoid an excessively high supersaturation level, crystal growth and secondary nucleation are the precipitation mechanisms, solution viscosity is kept low and the solid material can settle out in the sedimentation zone off the battery.

As can be seen from the dashed lines in Figure 7, once the peak value of the Al/XOH ratio has been passed, the ratio becomes constant, striking a balance between the rate of aluminum dissolution and precipitation and seed sedimentation rate. In this way no further passivation is threatened and the lifetime or discharge time of the battery is extended by a factor of 4 to 5 times that which can be obtained in the absence of added seed.

Certain preferred embodiments of the invention are shown in the following non-limiting examples.

Example 1

A test was conducted on electrolyte seeding using a single aluminum-air cell of the type shown in Figure 6. The cell was loaded with a 1/8" thick aluminum anode and the active electrode area was 268 cm<sup>2</sup>. A volume of 410 ml of 5 M NaOH and 0.010 M sodium stannate was circulated through the cell at 70°C at a flow rate of 4.5 l/min. The cell was connected to an external load of 21 millihours.

Figure 8 shows the voltage and current output of this cell, with a notable dip in voltage at 110 minutes due to a high supersaturation level in the electrolyte. Figure 9 shows a second test in the same cell with an identical

**SUBSTITUTE SHEET**

anode and electrolyte and under the same conditions except that 6 g of gibbsite seed was added at the 74-minute mark. There was no dip in the voltage and only a gradual voltage decrease after six hours.

5        Example 2

Further tests were carried out using the battery described in Figures 1-6 and using less than 1 micron gibbsite seed, these being to determine the effects of seed charge on anode passivation. The total electrolyte volume was 28 liters of 4.5 M KOH and 0.010 M sodium stannate. A first test was conducted with a seed charge of 100 grams and the second test was conducted at a seed charge of 1300 grams. The battery was designed to operate with an output of 1330 watts at 19 volts. The results obtained with the two different seed charges are shown in Figures 10 and 11.

Figure 10 is a plot of voltage as a function of discharge time and it will be seen that the voltage collapsed when the Al/KOH ratio reached 0.73 and remained very erratic thereafter. This indicates that insufficient seeding was used.

The results of a test conducted with a seed charge of 1300 grams are shown in Figure 11. It will be seen that a much more consistent high voltage was obtained over a long period of discharge.

25        Example 3

A further test was conducted to determine the effectiveness of  $\alpha$ -alumina as seeding agent. For the test, a supersaturated solution of caustic potassium aluminate was prepared using 4.5 M KOH and 3.27 M Al. A container holding 450 ml of the solution was placed in a constant temperature bath at 50°C and 10 g of  $\alpha$ -alumina particles were added. Stirring was conducted by magnetic stirrer bars. The solution conductivities were monitored with in-situ sensors, with a rise in conductivity signifying a decrease in dissolved alumina concentration.

-18-

The stirrer was started after about 130 minutes and stopped after about 240 minutes to determine the effectiveness of  $\alpha$ -alumina with and without stirring. The results, as shown in Figure 12, show that the conductivity  
5 declined after the stirrers were stopped.

SUBSTITUTE SHEET

## Claims:

1. A method of operating a metal-air battery of the type comprising an air cathode having opposed surfaces supported for simultaneous exposure of a first of said surfaces to air and a second of said surfaces to liquid electrolyte and a metal anode positioned in spaced  
5 juxtaposed relation to said second cathode surface to define therewith an anode-cathode gap for receiving electrolyte to form an anode-cathode pair electrically coupled by electrolyte,  
10 said method characterized by providing in said anode-cathode gap an alkaline electrolyte containing seed particles adapted to decrease passivation of the anode during discharge of the battery.
2. A method according to claim 1 wherein the seed is  
15 in the form of small particles of less than 1 micron.
3. A method according to claim 2 wherein the anode is aluminum or aluminum alloy.
4. A method according to claim 3 wherein the seeds comprise an aluminum oxide or salt.
- 20 5. A method according to claim 3 wherein the seeds comprise the mineral gibbsite.
6. A method according to claim 3 wherein the seeds comprise  $\alpha$ -alumina.
7. A method according to claim 6 wherein the  
25 electrolyte is stirred to hold the  $\alpha$ -alumina seeds in suspension.
8. A method according to claim 2 wherein the battery includes an electrolyte reservoir and the electrolyte is circulated from the reservoir through the anode-cathode  
30 gap.
9. A method according to claim 8 wherein the seed is added to the electrolyte after the battery has been discharged until the electrolyte has approached saturation.

10. A method according to claim 9 wherein the seed is added to the electrolyte by a time responsive automatic seed injector after a predetermined battery discharge time.
- 5 11. A metal-air battery comprising an air cathode having opposed surfaces supported for simultaneous exposure of a first of said surfaces to air and a second of said surfaces to liquid electrolyte and a metal anode positioned in spaced juxtaposed relation to said second
- 10 cathode surface to define therewith an anode-cathode gap for receiving electrolyte to form an anode-cathode pair electrically coupled by electrolyte,
- said battery containing an alkaline electrolyte and seed particles adapted to decrease passivation of the
- 15 anode during discharge of the battery.
12. A battery according to claim 11 wherein the seed particles are less than 1 micron.
13. A battery according to claim 12 wherein the anode is aluminum or aluminum alloy.
- 20 14. A battery according to claim 13 wherein the seeds comprise an aluminum oxide or salt.
15. A battery according to claim 14 wherein the seeds comprise the mineral gibbsite.
- 25 16. A battery according to claim 13 wherein the seeds comprise  $\alpha$ -alumina.
17. A battery according to claim 16 which includes a stirrer for stirring the electrolyte to hold the  $\alpha$ -alumina seeds in suspension.
- 30 18. A battery according to claim 9 which includes an electrolyte reservoir and means for circulating electrolyte from the reservoir through the anode-cathode gap.
19. A battery according to claim 18 herein the seed is retained in a time responsive automatic seed injector adapted to discharge seed into the reservoir at a
- 35 predetermined time during the discharge of the battery.

20. A battery according to claim 18 which comprises  
(a) a tank defining a reservoir for liquid electrolyte,  
(b) a plurality of metal-air cells mounted in  
side-by-side relationship above said reservoir with air  
5 gaps therebetween, each cell comprising a pair of  
spaced-apart flat side walls joined by end faces and top  
and bottom faces, said side walls including air cathodes,  
a metal anode mounted between and spaced from said flat  
side walls, an electrolyte inlet connector below the lower  
10 edge of the anode and an electrolyte outlet connector  
adapted to return electrolyte to the reservoir, and  
(c) circuit means for connecting said cells to an  
external load.

21. A battery comprising a cathode having opposed  
15 surfaces supported for exposure of one of said surfaces to  
liquid electrolyte and a metal anode positioned in spaced  
juxtaposed relation to said one cathode surface to define  
therewith an anode-cathode gap for receiving electrolyte  
to form an anode-cathode pair electrically coupled by  
20 electrolyte,

said battery containing liquid electrolyte and seed  
particles adapted to decrease passivation of the anode  
during discharge of the battery.

1/8

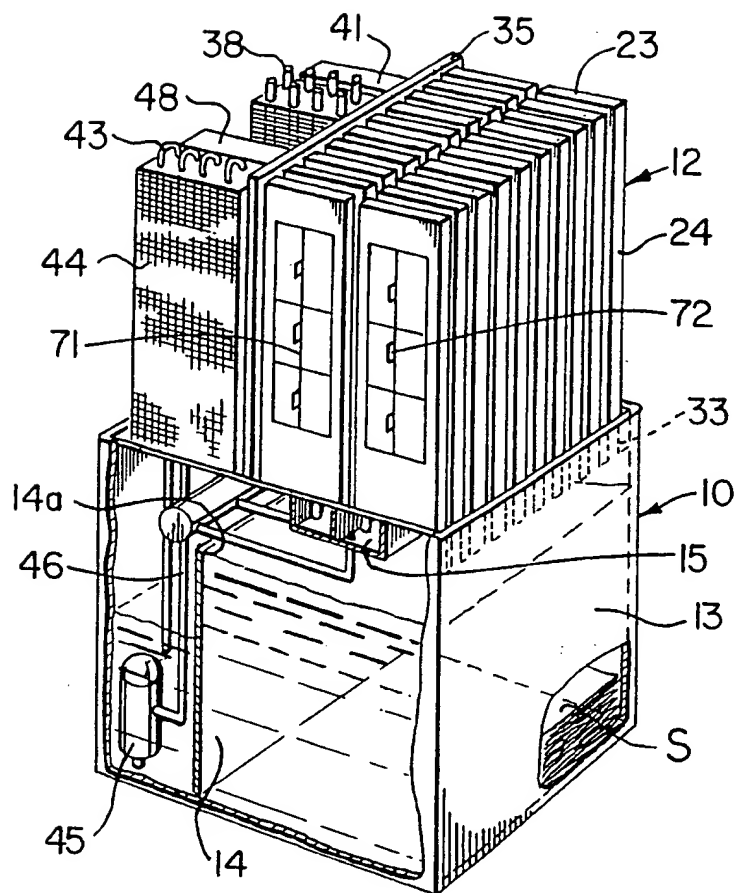


FIG. 1

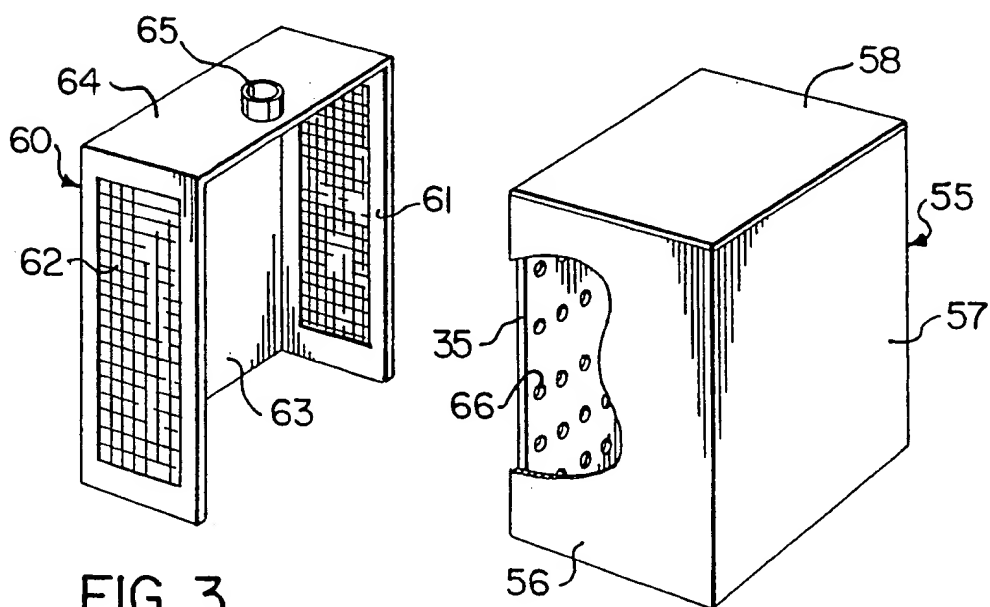


FIG. 2

FIG. 3

SIIRSTITIIE SHEFT



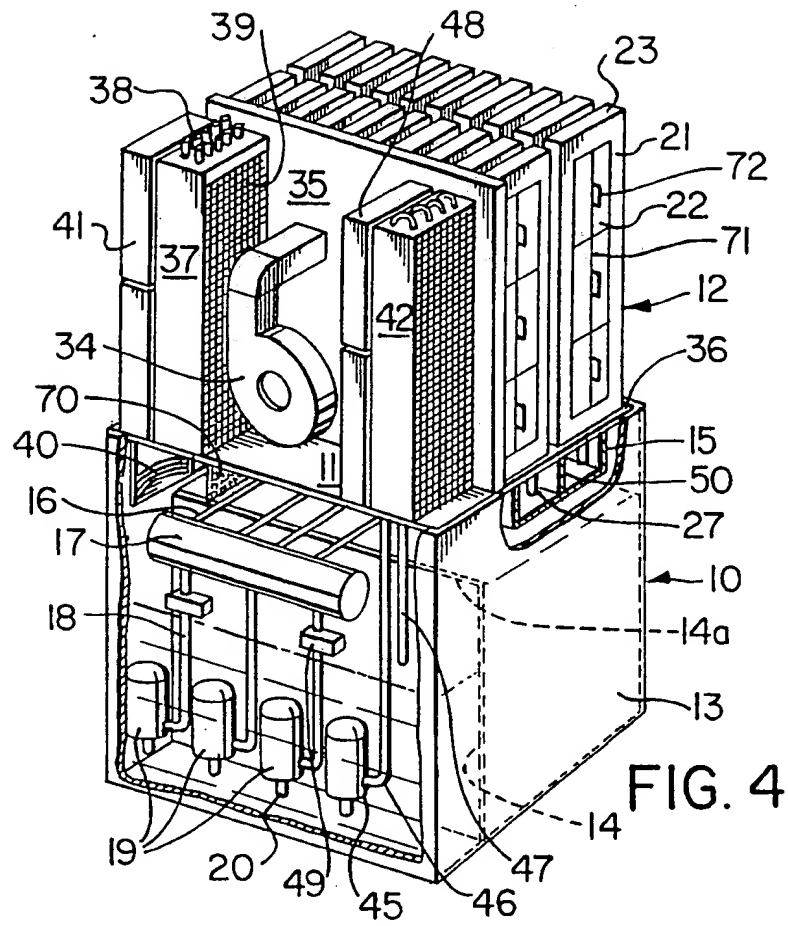


FIG. 4

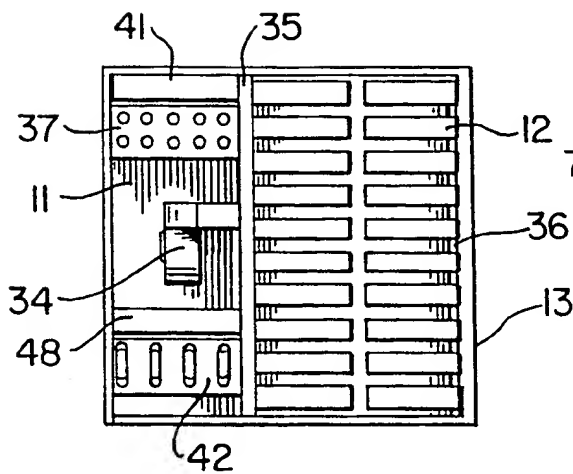


FIG. 5

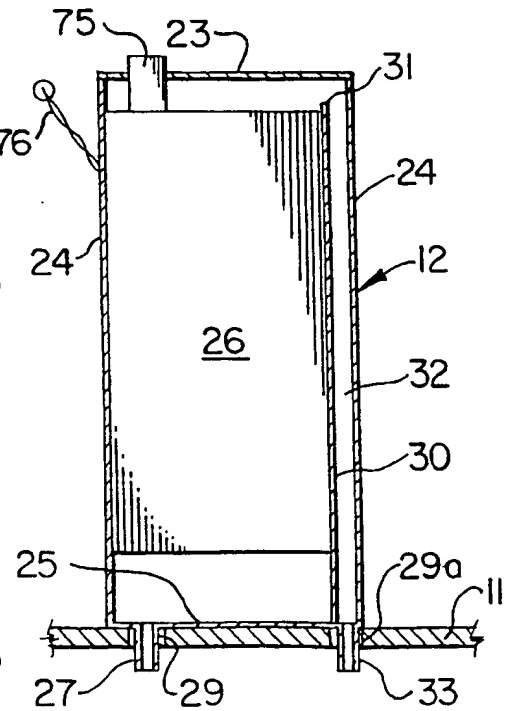


FIG. 6

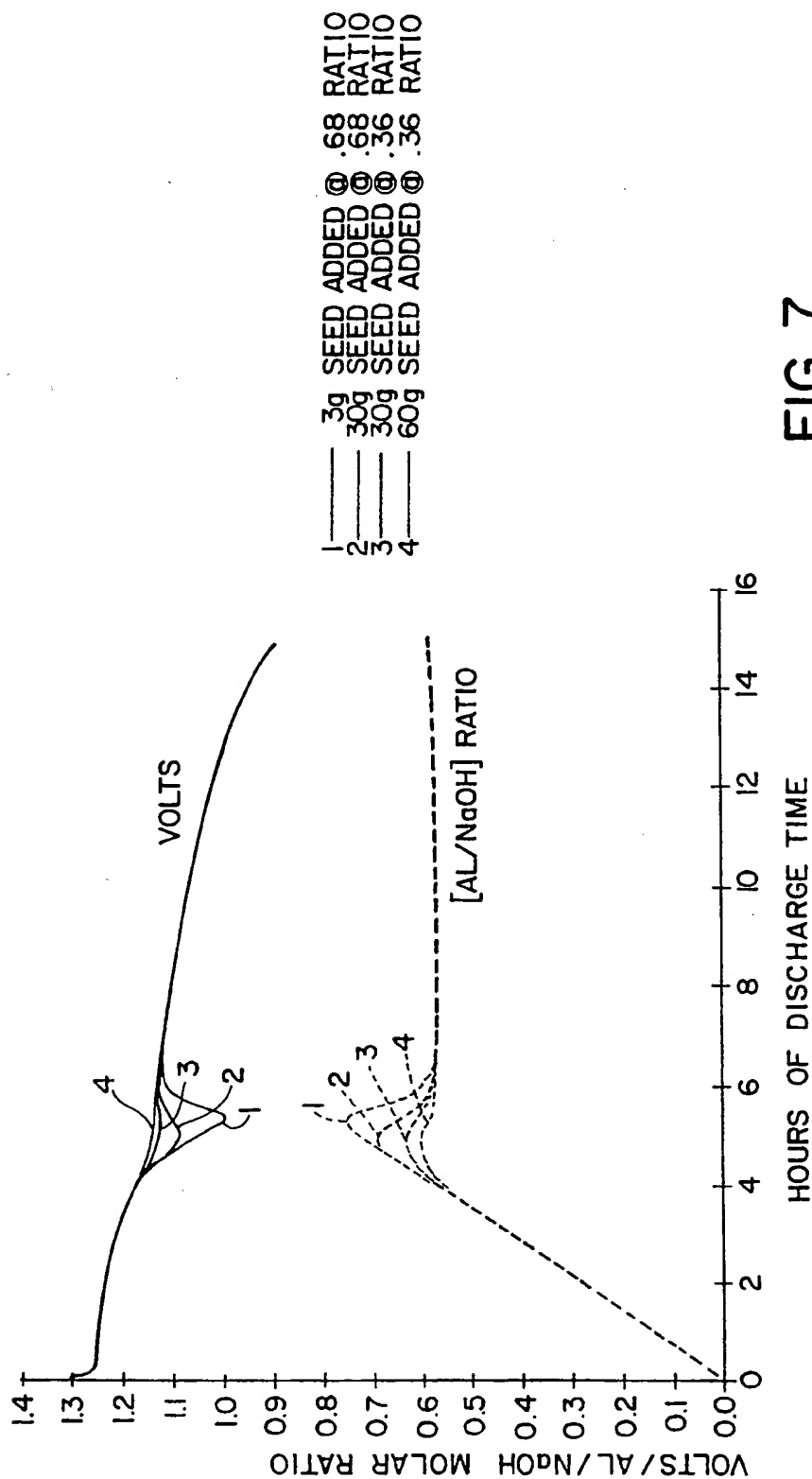


FIG. 7

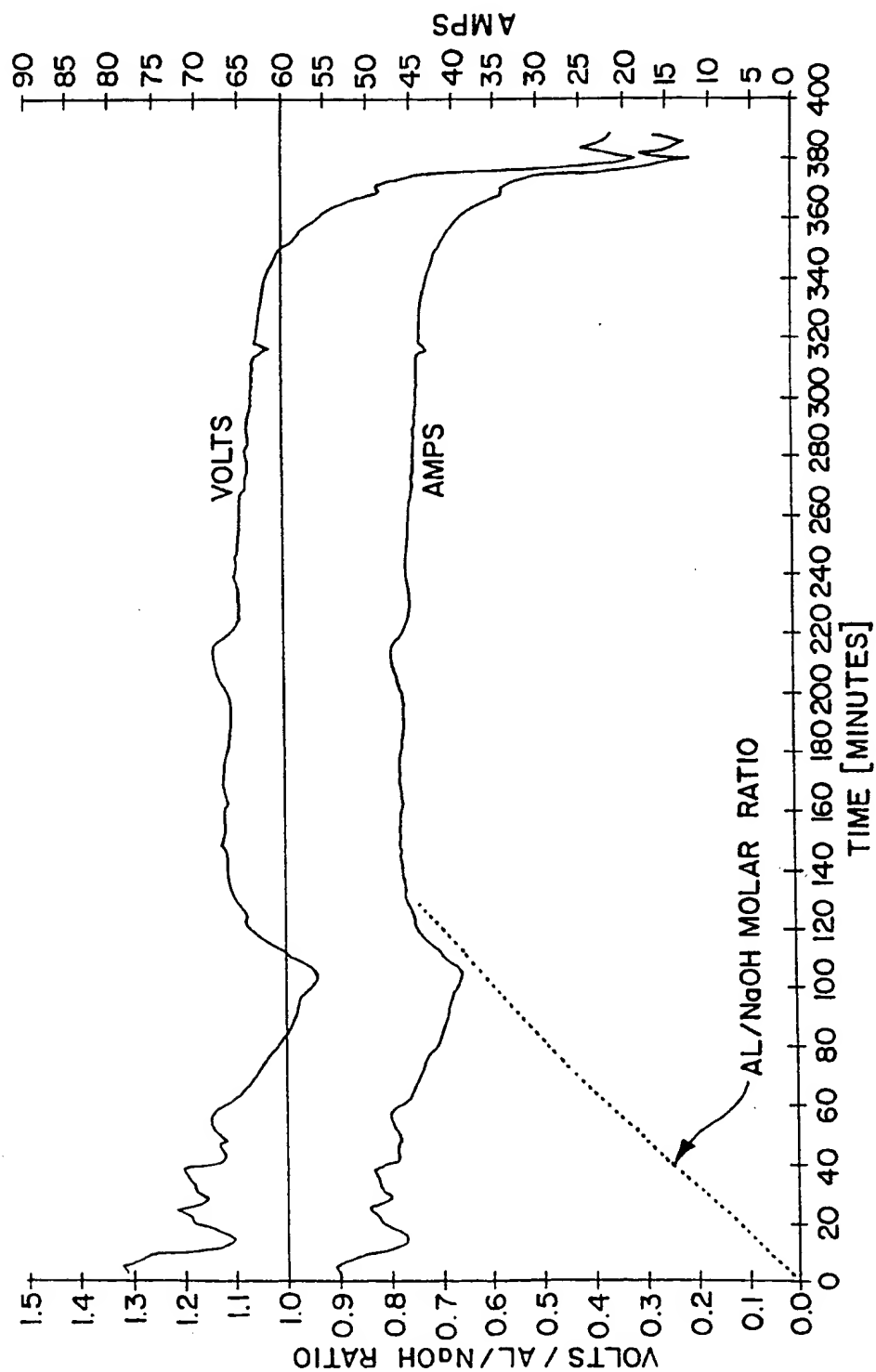


FIG.8

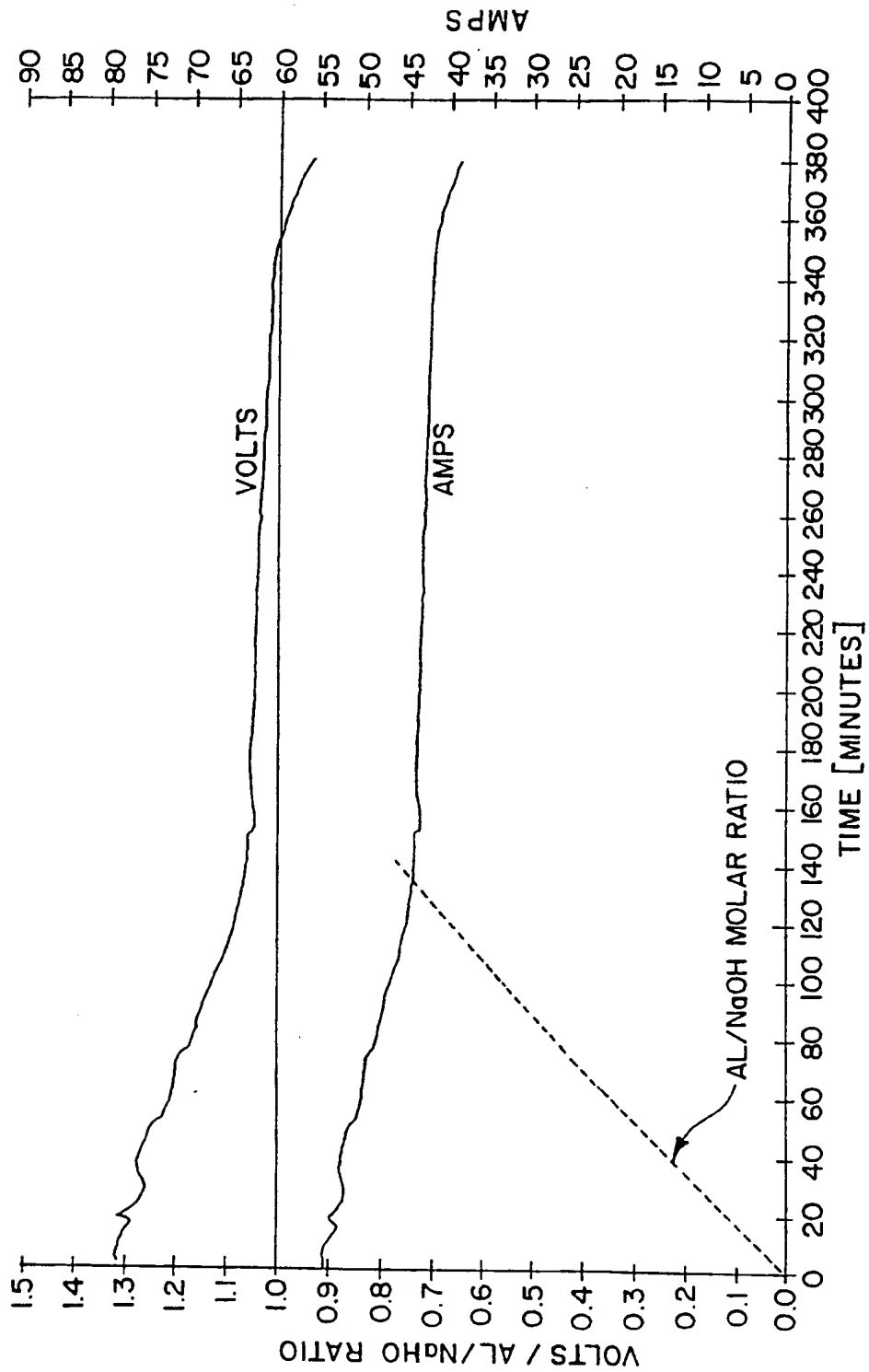


FIG. 9

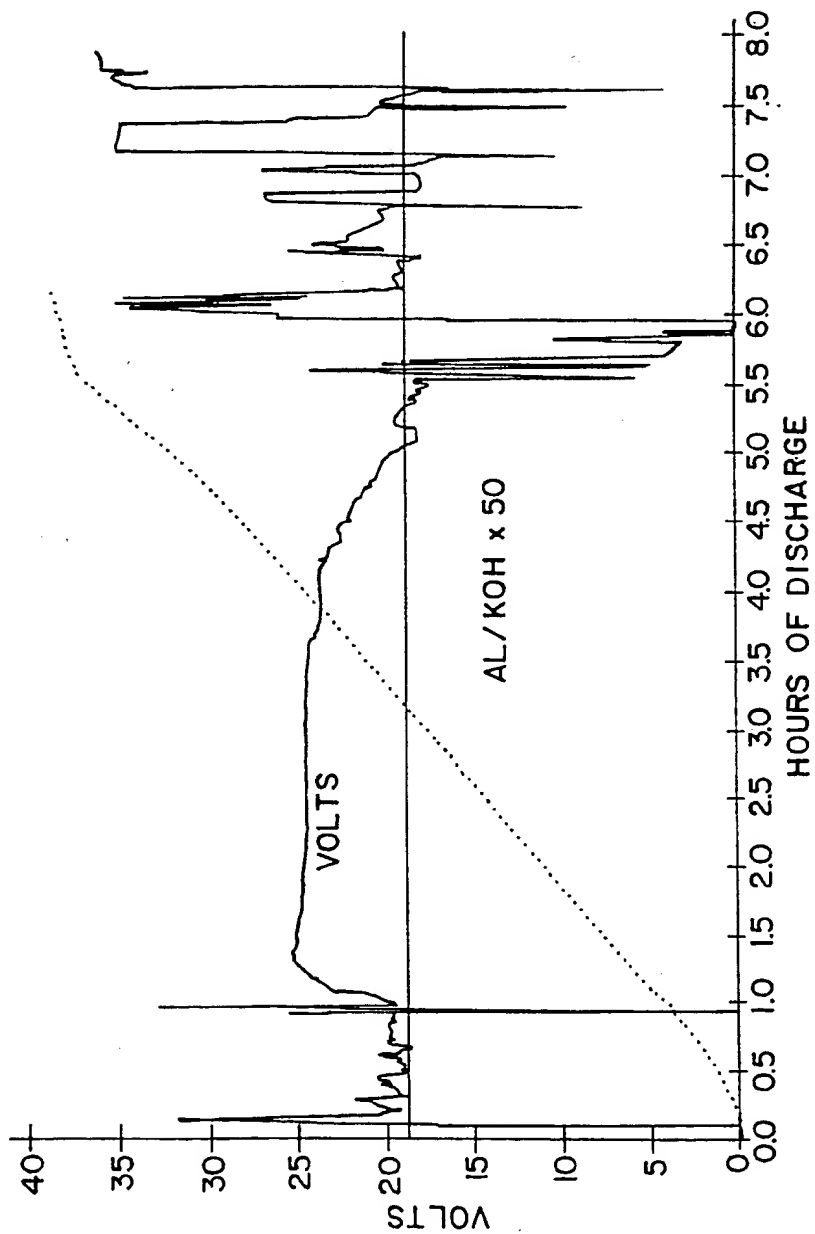


FIG. 10

7/8

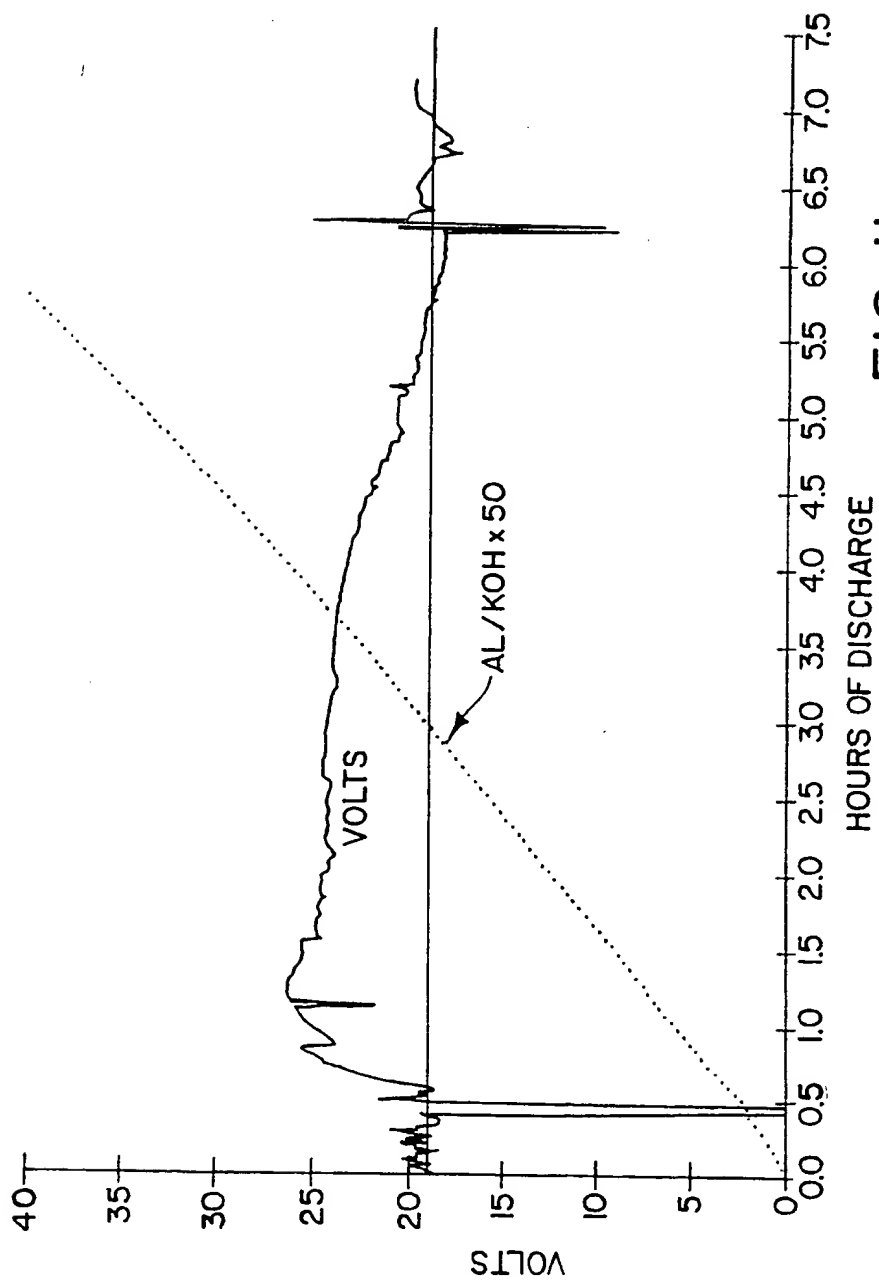


FIG. II

SUBSTITUTE SHEET

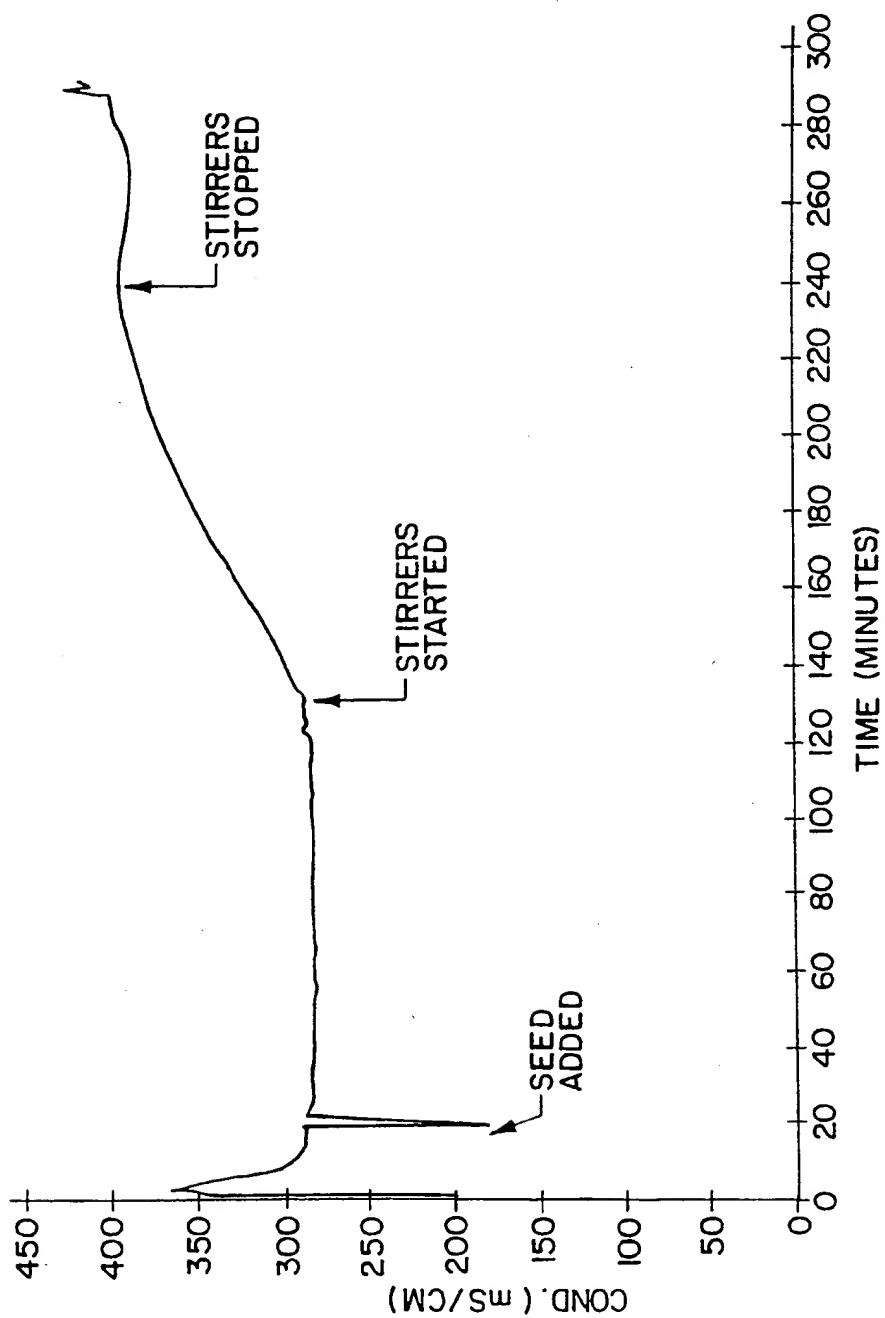


FIG. 12

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/CA 90/00096**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : H 01 M 6/50, H 01 M 12/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>5</sup>	H 01 M 6/50, H 01 M 12/06	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
E	EP, A, 0358335 (ALCAN INTERNATIONAL LIMITED) 14 March 1990 see abstract; page 4, line 23 - page 5, line 28; claims --	1-21
X	FR, A, 2153210 (ALSTHOM) 4 May 1973 see page 8, lines 7-17 --	1,11,21
X	US, A, 4735872 (ARTURO MAIMONI) 5 April 1988 see abstract; column 3, line 48 - column 4, line 32; column 7, line 12 - column 8, line 56 --	1-4,8,11-14,18
X	Proceedings of the 20th Intersociety Energy Conversion Engineering Conference, ./.	1-4,8,9,10-14,18,21
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
24th July 1990	23 AOUT 1990	
International Searching Authority	Signature of Authorized Official	
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR	



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	<p>Energy for the Twenty-First Century, SAE P-164, volume 2 of Three Volumes, August 1985, Society of Automotive Engineers, Inc., (Warrendale, PA), A. Maimoni: "Aluminum - Air power cell --a progress report", pages 2.14-2.20, see page 2.14, left-hand column, paragraph 2 - page 2.15, left-hand column, paragraph 1; page 2.16, left-hand column: integrated experiments</p> <p>--</p>	
X	<p>Chemical Abstracts, volume 92, no. 4, January 1980, (Columbus, Ohio, US), D.M. Drazic et al.: "Neutral electrolyte aluminum - air battery", see page 196, abstract 25477y, &amp; Power Sources 1978 (Pub. 1979). 7, 353-63 (Eng).</p> <p>--</p>	1-4,11-14,21
A	<p>EP, A, 0280764 (ELTECH SYSTEMS CORP.) 7 September 1988 see abstract; page 3, line 53 - page 5, example 1</p> <p>--</p>	1,8,11,13,18
A	<p>EP, A, 0265242 (ALCAN INTERNATIONAL LTD) 27 April 1988 see abstract; column 5, line 22 - column 8, line 4</p> <p>--</p>	11-21
A	<p>DE, A, 3239396 (ACCUMULATORENWERKE HOPPECKE CARL ZOELLNER &amp; SOHN GmbH) 26 April 1984 see the whole document</p> <p>--</p>	20,21
A	<p>EP, A 0240662 (INSTITUTE OF GAS TECHNOLOGY) 14 October 1987 see page 3, lines 21-46</p> <p>-----</p>	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

CA 9000096

SA 35817

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/08/90  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0358335	14-03-90	AU-A- 3937489 EP-A- 0354752	15-02-90 14-02-90
FR-A- 2153210	04-05-73	None	
US-A- 4735872	05-04-88	None	
EP-A- 0280764	07-09-88	US-A- 4719156 AU-A- 7942687 JP-A- 63224163 US-A- 4788111	12-01-88 08-09-88 19-09-88 29-11-88
EP-A- 0265242	27-04-88	AU-B- 598043 AU-A- 7999587 JP-A- 63126179 US-A- 4871627	14-06-90 28-04-88 30-05-88 03-10-89
DE-A- 3239396	26-04-84	FR-A,B 2535903 GB-A,B 2129199 JP-A- 59094386 US-A- 4490443	11-05-84 10-05-84 31-05-84 25-12-84
EP-A- 0240662	14-10-87	US-A- 4663250 JP-A- 62259352	05-05-87 11-11-87